A CONTRIBUTION TO THE CHEMISTRY
OF THE TELLURATES

EDGAR B. HUTCHINS

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INTRODUCTION.

The first systematic study of tellurium and its compounds was made by Berzelius in the early part of the last century. He showed that tellurium forms two oxygen acids, H_2TeO_3 and H_2TeO_4. Berzelius prepared telluric acid in the crystalline form and showed that it has the composition $H_2TeO_4.2H_2O$. He prepared a large number of the salts of both tellurous and telluric acids and found that nearly all of the metals yield insoluble compounds with these acids. Consequently the tellurates were largely obtained in the form of precipitates. Berzelius made quite a detailed study of some of these compounds. In the case of others, however, the tellurate was prepared and but little more is recorded concerning it. The work of Berzelius is of great importance in that it has not only furnished us with a large number of facts concerning these compounds but also paved the way for a fuller investigation of their properties by later chemists.

Oppenheim, Becker, Staudenmaier, Retgers, Mylius, and Gutbier have each made important contributions to our knowledge of telluric acid and its salts.

All of the alakli metals, sodium, potassium, rubidium, and caesium yield soluble crystalline tellurates and these have received the attention of investigators to a greater extent than have the tellurates of the heavy metals. Indeed many of the tellurates that were obtained as precipitates by Berzelius appear not to have been studied at all by later investigators. An examination of the literature on the tellurates shows that detailed knowledge of most of them is wanting. Many of the properties that have been observed appear to be those of mixtures. This is doubtless

due to the fact that telluric acid possesses weak acid properties and has a great tendency to form basic salts, particularly with the heavy metals, and, in general, to form complex salts. It is frequently found that the line of demarcation between two of the tellurates as they separate from solution is so narrow that one salt is contaminated by another and sometimes by a third or a fourth. The tellurates of the alkali metals are the only ones that have hitherto been described as crystalline.

The following work was undertaken with a view of preparing a number of the tellurates and studying their properties. The work has been confined for the most part to the salts of potassium, silver, and mercury. Careful attention has been devoted to their preparation in the crystalline form. The ease with which the tellurates of silver and mercury are decomposed by water has made this problem particularly difficult. For the most part the salts appear at first as amorphous precipitates of varying composition and quickly alter in the mother liquor, their subsequent composition depending on the conditions in the solution.

TELLURIC ACID.

Berzelius[1] prepared telluric acid by oxidizing tellurium dioxide in alkaline solution with chlorine. From this solution he precipitated barium tellurate by means of barium chloride and subsequently treated the barium salt formed, with sulphuric acid. Sulphuric acid liberates free telluric acid from barium tellurate, insoluble barium sulphate being formed at the same time. Berzelius also oxidized tellurium dioxide by fusing it with potassium nitrate. From the potassium tellurate thus formed, he obtained barium tellurate from which, in turn, he liberated the free acid by means of sulphuric acid.

Oppenheim[2] obtained the acid by fusing tellurium dioxide with potassium hydrate and potassium chlorate. He used the method of Berzelius for preparing the free acid from the alkali tellurate.

Becker[3] dissolved tellurium in nitric acid and oxidized the solution by means of lead peroxide. The lead tellurate obtained was decomposed by sulphuric acid.

Gutbier[4] and Resenscheck have shown that telluric acid can be prepared by oxidizing tellurium dioxide by means of hydrogen peroxide in a solution which is strongly alkaline with sodium or potassium hydroxide. The alkali tellurate which is obtained in this manner is treated with nitric acid and the telluric acid obtained in the free condition.

The telluric acid used in this work was obtained by purifying and oxidizing electrolytic tellurium prepared by the Baltimore Copper Co. This tellurium contains silver, copper, and selenium as its principal impurities. The acid was prepared by the method described by Staudenmaier.[5] By this method free telluric acid is obtained by oxidation of tellurous acid by means of chromic acid. In many respects this method is superior to those in which sulphuric acid is used to set the telluric acid free. The yield is greater, the operaton is more direct, and the sulphuric and selenic

[1] Pogg. Ann., Vol. 32, p. 23.
[2] Jour. f. pr. Chem., Vol. 71, p. 266.
[3] Ann. Chem., Vol. 180, p. 256.
[4] Zeit. f. anorg. Chem., Vol. 40, p. 260.
[5] Zeit. f. anorg. Chem., Vol. 10, p. 189.

acids are eliminated in one of the first steps of the process which consists in purifying tellurium dioxide. These acids are apt to contaminate telluric acid prepared by the other methods, unless special precautions are taken.

The method as carried out in this work is as follows:

Tellurium is dissolved in aqua regia and the resulting solution freed from nitric acid by evaporating with excess of hydrochloric acid. After the hydrochloric acid solution has been diluted and filtered the tellurium is precipitated by means of sodium acid sulphite and repeatedly washed with hot water. The moist tellurium is oxidized with nitric acid and the resulting basic nitrate purified by recrystallization.

The purified basic nitrate is covered with several times its bulk of dilute nitric acid. A little more chromic acid is added to the solution than is required by the equation $3TeO_2+2CrO_3+3H_2O=3H_2TeO_4+Cr_2O_3$. When the mixture is boiled for some time the tellurium dioxide is completely oxidized to telluric acid according to the above equation. The solution is then concentrated over the water bath until a crystalline crust begins to form and allowed to cool slowly. The telluric acid separates as a compact crystalline layer which is easily removed from the solution and rinsed to free it from the mother liquor. If the nitric acid solution to which the chromic acid has been added is quite concentrated, telluric acid will separate from the hot solution in the form of fine crystals. The solution is cooled, decanted, and again concentrated over the water bath until crystals form. This operation is repeated as long as telluric acid separates from the mother liquor.

The telluric acid, which is green from the presence of chromium nitrate, is dissolved in hot water and recrystallized. If a white residue remains when the acid is dissolved, it is an indication that the amount of chromic acid was insufficient to oxidize all of the tellurium dioxide. A residue may remain even when the hot nitric acid solution is clear. This is due to the fact that tellurium dioxide is much more soluble in hot nitric acid than in cold, and so may separate with the telluric acid when the solution is cooled. In order to remove the chromium nitrate from the telluric acid and obtain a pure white product the acid must be recrystallized

from ten to twenty-five times, depending upon the amount of the chromium salt present.

It has been found possible to prepare fifteen hundred grams of the recrystallized acid in six weeks. The yield is about 80%. Telluric acid remains in the mother liquor along with the chromium nitrate, from which it cannot be readily separated as the solution becomes syrupy upon evaporation.

Telluric acid is readily soluble in either hot or cold water. It is much more soluble in hot water than in cold. Its solubility is decreased by the addition of nitric acid. This fact may be made use of in the separation of telluric acid from chromium nitrate. When concentrated nitric acid is added to a concentrated solution of these compounds telluric acid is precipitated; the chromium nitrate being soluble in nitric acid, remains in solution. If a solution of telluric acid is concentrated rapidly it does not crystallize but appears as a syrupy or gummy mass.

Telluric acid is dimorphous[6] crystallizing in the hexagonal-rhombohedral and isometric systems. It usually crystallizes from its solutions in the rhombohedral system but regular octahedra are sometimes formed. The crystals are colorless and transparent. They have the composition represented by the formula $H_2TeO_4.2H_2O$.

Staudemaier[7] describes a second hydrate of telluric acid having the composition $H_2TeO_4.6H_2O$ which he obtained by cooling an aqueous solution of telluric acid to zero.

Telluric acid is a weak acid showing but a feeble reaction to litmus. Gutbier[8] found that telluric acid has about the same molecular conductivity as hydrocyanic acid or hydrogen sulphide. He determined the molecular weight of telluric acid by the freezing point method. From the results which he obtained he concludes that telluric acid should be represented by the formula $Te(OH)_6$ and not $H_2TeO_4+2H_2O$.

When heated above 110° telluric acid loses water. According to Gutbier[9] constant weight is obtained at 145°. He shows that the loss in weight at that temperature is not as great as that re-

[6] Gutbier—Studien über das Tellur, p. 18.
[7] l. c.
[8] l. c.
[9] Studien über das Tellur., p. 16.

quired by the change of $H_2TeO_4.2H_2O$ to H_2TeO_4. Experiments carried out during the progress of this work have given similar results to those obtained by Gutbier.

Mylius[10] states that $H_2TeO_4.2H_2O$ is changed to $(H_2TeO_4)_n$ at about 140°. He calls the polymerized acid allotelluric acid and shows that its solutions have a much greater conductivity than the acid that has not been dehydrated. The conductivity of solutions of allotelluric acid, according to Mylius, diminishes upon standing. This may indicate that the acid gradually assumes the composition H_6TeO_6 when in solution.

While telluric acid may be considered a weak acid, a hot aqueous solution of it will attack many metals such as silver, mercury, lead, bismuth, copper, zinc, arsenic, antimony, tin, aluminum, cadmium, and nickel. A number of these metals are attacked by a cold solution of the acid.

SALTS OF TELLURIC ACID.

The types of salts that telluric acid forms may be represented as follows: $(2M_2O.3TeO_3)$, $(M'_2O.2TeO_3)$, $(M'_2O.TeO_3)$, $(3M'_2O.2TeO_3)$, and $(3M'_2O.TeO_3)$. Crystalline salts of all of these types are now known. With the possible exception of mercuric orthotellurate[11] (Hg_3TeO_6) no anhydrous crystalline salt has been described. It is claimed by Nandl and von Lang[12] that K_2TeO_4 exists as a crystalline salt in the anhydrous condition but its existence has been disputed[13] by Retgers, Rammelsberg, Staudenmaier, and Gutbier.

Berzelius considered telluric acid a dibasic acid and accordingly called salts of the type M'_2TeO_4 normal tellurates and salts of the other types basic or acid tellurates according as they contain more or less metallic oxide than the normal salt. This nomenclature has been universally adopted in describing the tellurates and is adhered to in the following description. However,

[10] Ber., Vol. 34, II, p. 2208.
[11] New salt.
[12] Wiener Akad. Ber., Vol. 43, p. 117.
[13] Gutbier, Studien über das Tellur., p. 36.

salts of the type M'_6TeO_6 are termed ortho-tellurates from their evident relation to orthotelluric acid H_6TeO_6.

We have both amorphous and crystalline salts of the type M'_6TeO_6 such as Ag_6TeO_6,[14] Hg''_3TeO_6,[15] Cu_3TeO_6,[16] and Zn_3TeO_6.[16] These salts appear to be derived from the hexabasic acid H_6TeO_6 which is identical in composition with ordinary telluric acid.

The crystalline salts of the type $M_2O.TeO_3$ contain two or more molecules of water, for example, ($Na_2O.TeO_3.2H_2O$),[17] ($K_2O.TeO_3.2H_2O$),[18] ($Cs_2O.TeO_3.3H_2O$),[19] ($Rb_2O.TeO_3.3H_2O$),[19] ($Ag_2O.TeO_3.2H_2O$),[20] ($HgO.TeO_3.2H_2O$).[20] These compounds may be considered acid salts of orthotelluric acid of the types—($Na_2H_4TeO_6$), ($K_2H_4TeO_6$), ($Cs_2H_4TeO_6.H_2O$), ($Ag_2H_4TeO_6$), (HgH_4TeO_6).

Likewise the silver salt ($3Ag_2O.2TeO_3.3H_2O$),[20] which according to the nomenclature in vogue is a basic salt, may be considered an acid salt of the type $Ag_3H_3TeO_6$.

This view of the tellurates finds some confirmation in the experiments of Gutbier and Mylius on the molecular weight and electrical conductivity of telluric acid. It is also supported by the behavior of the hydrous tellurates when heated. Gutbier[21] has shown that the alkali tellurates decompose with the liberation of oxygen before the water which they contain is entirely driven off. The silver salts mentioned do not give up all of their water until a temperature of 200°.is reached. Oxygen is evolved from these salts at a temperature only a few degrees above this point.

Some of the crystalline tellurates contain more water than is required to make them derivatives of orthotelluric acid; such salts are $K_2TeO_4.5H_2O$[22] and $HHgTeO_4.3H_2O$.[23] These com-

[14] Amorphous, Berzelius.
[15] Crystalline, new salt.
[16] Amorphous, new salts.
[17] Berzelius.
[18] Retgers, Zeit. f. phys. Chem., Vol. 10, p. 536.
[19] Norris and Kingman, Am. Chem. Jr., Vol. 26, p. 320.
[20] New salts.
[21] Studien über das Tellur., p. 34.
[22] Berzelius.
[23] New salt.

pounds may be considered acid salts containing water of crystallization, thus,—$K_2H_4TeO_6.3H_2O$ and $HgH_5TeO_6.H_2O$.

Such crystalline salts as $CsHTeO_4.\frac{1}{2}H_2O$ and $RbHTeO_4.\frac{1}{2}H_2O$[24] would have to be considered salts of a higher acid, as $H_6Te_2O_9$.

Corresponding to the type M'_2TeO_4 a large number of anhydrous tellurates have been prepared but they are all amorphous. These salts may also be considered metatellurates. Their relation to orthotelluric acid is similar to that which the metaborates bear to orthoboric acid. It is problematical how much water these salts would contain were it possible to prepare them in the crystalline condition.

In addition to the types of tellurates enumerated above a number of tellurates corresponding to $M_2Te_2O_7$ have been prepared. They have been called the pyrotellurates. Berzelius also described the salts $Na_2O.4TeO_3.5H_2O$ and $K_2O.4TeO_3.4H_2O$.

METHODS OF ANALYSIS.

Many of the metals may be precipitated from solutions of the tellurate under conditions that will allow all of the tellurium to remain in the filtrate. Thus silver was determined in some cases by precipitation as chloride from a solution of the tellurate in dilute nitric acid.

In the analysis of the tellurates of those metals where chlorides are not volatile below a red heat the tellurium has been volatilized as $TeO_2.2HCl$ and the non-volatile chloride weighed. This method of determining the metal is preferred to the method of precipitation because it is less time-consuming; there are fewer operations required for the analysis and less opportunity for experimental error. In cases where it is applicable, that is, where the chloride of the metal is not readily volatile, it gives at once a clean separation of the metal from telluric acid. Moreover the tellurium is obtained in a suitable solution for precipitation with sulphur dioxide.

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[24] Norris and Kingman, l. c.

Professor Lenher[25] has shown that when dry hydrochloric acid gas is passed over a tellurite heated to a temperature somewhat below redness the tellurium is completely volatilized as $TeO_2.2HCl$. If the chloride of the metal is not volatile it remains in the boat. He has employed this method in the analysis of a number of the tellurites. The method has been found to work equally well for the analysis of salts of telluric acid. Following is a description of the method as it has been carried out.

A sample of the tellurate to be analyzed is placed in a porcelian boat which has been weighed. The boat is loosely covered with a thin glass plate and introduced into a hard glass tube. Hydrochloric acid gas is generated by allowing concentrated hydrochloric acid to drop slowly into a flask containing concentrated sulphuric acid. In this manner a steady stream of the gas is provided. The gas after having been dried by sulphuric acid is passed through the tube, which is heated to a dull red heat. The hydrochloric acid decomposes the tellurate with the formation of the chloride of the metal, chlorine, and $TeO_2.2HCl$ according to the following equation: $M_2TeO_4 + 6HCl = 2MCl + 2Cl + TeO_2.2HCl + 2H_2O$. The tellurium compound sublimes upon the cold part of the tube in the form of crystalline flakes leaving only the chloride of the metal in the boat. The boat is removed from the tube, cooled in a desiccator and weighed. The escaping hydrochloric acid gas is collected in a receiver containing cold water. The tellurium may be washed from the tube into the receiver with hydrochloric acid and precipitated with sulphurous acid. Tellurium was repeatedly determined by this method.

The method which Norris and Kingman[26] used in the analysis of the tellurates was largely employed for the estimation of tellurium. This method depends upon the fact that hot aqueous hydrochloric acid completely reduces telluric acid to tellurium tetrachloride with the liberation of free chlorine, according to the following equation: $H_2TeO_4 + 6HCl = Cl_2 + TeCl_4 + 4H_2O$. This reaction goes on only slowly, if at all, in the cold. The analysis is carried out as follows:

[25] Unpublished notes.
[26] l. c.

The sample to be analyzed is placed in a small round-bottomed flask together with a small piece of magnesite. About fifty cubic centimeters of concentrated hydrochloric acid is added. The solution is heated until about one-third of it has distilled over, the distillate being collected in a solution of potassium iodide kept cool by a freezing mixture. The liberated iodine is titrated with a solution of sodium thiosulphate.

To test the accuracy of this method a weighed amount of recrystallized telluric acid was decomposed by hydrochloric acid. The chlorine liberated by the reaction was absorbed by a solution of potassium iodide and the liberated iodine titrated with a solution of sodium thiosulphate. The solution of sodium thiosulphate was standardized against pure iodine. 0.4465 grams of telluric acid liberated chlorine equivalent to 0.2482 grams of tellurium. $H_2TeO_4.2H_2O$ requires 55.56% Te; found 55.59%.[27]

If it is desired, the metal may be determined in the solution after the tellurate has been reduced and the chlorine distilled. This was done in some cases where the amount of material at hand was small.

Tellurium can be determined in telluric acid or its salts much more quickly by this method than by any method requiring precipitation of elementary tellurium. The entire determination requires less than one hour. Moreover the method has proven more reliable as carried out in this work than precipitation of elementary tellurium by sulphur dioxide.

In separating mercury from telluric acid use has been made of the fact that tellurium sulphide is soluble in a solution of ammonium sulphide. The tellurate of mercury is dissolved in dilute hydrochloric acid. Mercurous compounds are oxidized by chlorine or bromine water. If the acid solution is saturated with hydrogen sulphide in the cold only a trace of telluric acid is reduced.[28] The solution of telluric acid is then decanted from the

[27] All calculations have been made on the basis of Te = 127.6.

[28] Brauner, Jr. Chem. Soc., Vol. 67, p. 545.

precipitated HgS. The precipitate is washed by decantation with hydrogen sulphide water to free it from telluric acid, and then digested with ammonium sulphide to remove the trace of tellurium precipitated with the mercuric sulphide.

Instead of decanting the solution of telluric acid from the precipitated mercuric sulphide it may be made strongly ammoniacal and saturated with hydrogen sulphide. Telluric acid is reduced at once by hydrogen sulphide in alkaline solution. The precipitate that is formed dissolves immediately in ammonium sulphide forming a yellow solution. All of the tellurium will now be found in the solution. The mercuric sulphide is washed with a solution of ammonium sulphide and hydrogen sulphide water, dried at 110° and weighed.

Water was determined in most cases by heating the tellurate in a current of dry air and collecting the water in sulphuric acid.

THE TELLURATES OF SILVER.

NORMAL SILVER TELLURATE.

Berzelius[29] describes normal silver tellurate (Ag_2TeO_4) as a dark yellow precipitate. He states that he obtained this compound in the form of bulky flakes by adding a concentrated solution of silver nitrate to a solution of normal potassium tellurate. If the precipitate is treated with boiling water it is converted into a brown basic silver tellurate.

Gutbier[30] states that it is hardly possible to prepare normal silver tellurate in pure condition by the method described by Berzelius. According to Gutbier the precipitate obtained from concentrated solutions of silver nitrate and potassium tellurate is always contaminated with a larger or smaller amount of basic silver tellurate.

It has not been found possible to prepare normal silver tellurate (Ag_2TeO_4) in pure condition by precipitation as described by Berzelius. When solutions of silver nitrate and normal potassium tellurate are brought together, the precipitate contains basic silver tellurate. The formation of a basic salt may be obviated by using an acid tellurate of potassium, for example, $KHTeO_4$, in place of the normal tellurate. But under these conditions the precipitate may contain an excess of telluric acid. Moreover when the precipitate is washed it is decomposed forming a basic tellurate of silver.

It has been found possible to prepare well crystallized normal silver tellurate. Crystals of this salt are not rapidly attacked by cold water and may be obtained free from basic salts.

Silver tellurate has been obtained by the following methods: the action of telluric acid upon silver oxide; the double decomposition of a soluble silver salt with a soluble tellurate or telluric acid; the action of telluric acid upon metallic silver.

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[29] Pogg. Ann. d. Phys. u. Chem., Vol. 32, p. 577.
[30] Zeit. f. Anorg. Chem., Vol. 31, p. 340.

Action of Telluric Acid on Oxide of Silver.

When silver oxide is treated with a slight excess of a solution of telluric acid, normal silver tellurate is formed according to the equation: $Ag_2O + H_2TeO_4.2H_2O = Ag_2TeO_4.2H_2O + H_2O$.

The silver tellurate obtained by this method has quite different physical properties from the yellow precipitate described by Berzelius and Gutbier. It is a heavy granular powder nearly white in color. It has the composition $Ag_2TeO_4.2H_2O$. It is much more stable in the presence of water than the yellow precipitate hitherto described. When the powder is heated to 100° it loses a part of its water and assumes a brown color; but it does not give up all of its water until a much higher temperature is reached. It is soluble in ammonium hydrate, sodium thiosulphate, and the acids. The white powder reacts with silver oxide suspended in hot water to form a brown basic tellurate of silver.

If a solution of $Ag_2TeO_4.2H_2O$ in acetic or nitric acid is evaporated to dryness *in vacuo* telluric acid and silver acetate or nitrate are formed. When the salt is strongly compressed between steel rolls it detonates and assumes a brown color. The same property is possessed by the tellurates of mercury. This work will be continued later.

For analysis the salt was dried over sulphuric acid and dissolved in dilute nitric acid. The silver was precipitated from the solution by dilute hydrochloric acid. The filtrate was evaporated with an excess of hydrochloric acid to free it from nitric acid. The tellurium was precipitated in the hydrochloric acid solution by sulphurous acid.

Analysis gave the following results:

0.9597 grams gave 0.6172 grams AgCl and 0.2755 grams Te.
0.9051 grams gave 0.0724 grams H_2O.

	Ag	Te	H_2O
Calculated for $Ag_2TeO_4.2H_2O$ —	48.68%	28.77%	8.11%
Found	48.40%	28.06%	7.99%

Crystalline $Ag_2TeO_4.2H_2O$.

It has been found possible to obtain crystals of normal silver tellurate by slowly evaporating a solution made by bringing together dilute solutions of telluric acid and silver acetate containing free acetic acid. The dilute acetic acid holds the tellurate of silver in solution and allows it to crystallize as the solution is evaporated. The acetic acid solution must be quite dilute, as a strong solution of the acid prevents the formation of silver tellurate.

When solutions of silver acetate and telluric acid of moderate concentration are brought together a lemon yellow precipitate is formed. The precipitate closely approximates Ag_2TeO_4 in composition. When a solution of silver acetate containing 2.0 grams of silver acetate and a few drops of free acetic acid per liter, is mixed with an equal volume of a solution of telluric acid containing 1.4 grams of the acid per liter, no precipitate is formed. When such a solution is allowed to evaporate in the dark at room temperature yellow crystals of $Ag_2TeO_4.2H_2O$ are formed. The free telluric acid in the solution prevents the decomposition of the normal salt by the water. Only small amounts of the salt have been prepared in this manner. Larger quantities of the salt are more conveniently prepared in the following manner:

Upon adding an excess of a solution of silver nitrate to a concentrated solution of potassium tellurate containing a little free acetic acid a yellow or brown precipitate is formed. Analysis showed that this precipitate approximates normal silver tellurate in composition. Its exact composition depends largely on the concentration of the solution. It was observed that when such a solution is allowed to remain in contact with the precipitate for a few hours a heavy yellow salt separates at the bottom of the beaker. The salt is composed of distinct crystals of a straw yellow color. As the crystals have a much higher specific gravity than the amorphous precipitate, they can easily be separated from it by elutriation. If the precipitate is allowed to remain in the mother liquor for several days, red crystals of a basic silver tel-

lurate will usually be found among the yellow crystals of the normal salt.

Analysis of the yellow crystals gave the following results:

0.7638 grams gave 0.0605 grams H_2O.

0.4847 grams gave 0.3117 grams AgCl.

0.4980 grams when heated with hydrochloric acid gave sufficient chlorine gas to liberate 0.2828 grams of iodine from potassium iodide.

	H_2O	Ag	Te
Calculated for $Ag_2TeO_4.2H_2O$	8.11%	48.68%	28.77%
Found	7.92%	48.41%	28.57%

In this analysis the silver was precipitated with hydrochloric acid from a dilute nitric acid solution of the salt.

Silver acetate or sulphate may be used instead of silver nitrate for the preparation of the salt by double decomposition with potassium tellurate and subsequent change of the amorphous precipitate to the crystalline salt. Likewise the free acetic acid may be replaced by nitric acid, or the acid may be omitted altogether. The salt crystallizes much better, however, when the solution contains free acid.

$Ag_2TeO_4.2H_2O$ crystallizes in the orthorhombic system. The crystals resemble those of sulphur both in the forms that occur and in the axial ratios. They are insoluble in hot or cold water but soluble in ammonia, potassium cyanide, sodium thiosulphate, and nitric, acetic and sulphuric acids. Concentrated nitric, acetic, or sulphuric acids completely decompose silver tellurate, giving free telluric acid and the corresponding silver salt.

When crystals of the normal salt are allowed to remain for some time in contact with a cold solution of a silver salt, red crystals of the basic tellurate $3Ag_2O.2TeO_3.3H_2O$ are formed. The change is much more rapid in a ten per cent solution of silver nitrate at a temperature of 50° than in the cold. It takes place very slowly even in cold water.

Crystals of $Ag_2TeO_4.2H_2O$ darken slowly when exposed to the light. When the powdered crystals are compressed between steel rolls they detonate. When heated above 100° the crystals lose water and take on a brilliant purplish black lustre. They maintain this lustre until a temperature of about 200° is reached.

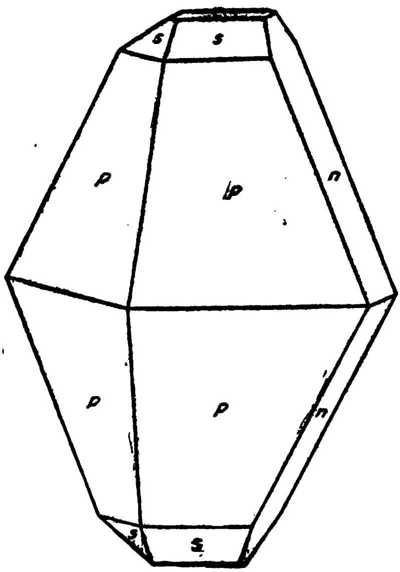
As the temperature is raised still higher oxygen is evolved, the mass assumes a gray brown color and fuses. If the mass is allowed to cool as soon as it fuses, it becomes black and crystalline, but if it is heated to bright redness it is completely changed to silver tellurite, which is white when cold.

The crystalline normal salt may be prepared entirely free from basic silver tellurate by allowing the precipitate obtained by mixing solutions of silver nitrate and acid potassium tellurate to remain in the mother liquor until it assumes the crystalline form.

$Ag_2TeO_4.2H_2O$

Orthorhombic. Axes—a :b :c = 0.722 : 1 : 2.107.[31]

pp‴, $111 : 1\bar{1}1 = 111° 26'$.
pp′, $111 : \bar{1}11 = 77° 25'$.
cp, $001 : 111 = 105° 40'$.
cn, $001 : 011 = 115° 29'$.
cs, $001 : 113 = 103° 02'$.



[31] The author is indebted to Professor Hobbs for his kindly advice in that part of this work which deals with the crystallography of the tellurates.

The crystals that were used for measurement were obtained by double decomposition of solutions of silver nitrate and potassium tellurate containing a little free acetic or nitric acid. The amorphous precipitate that formed on mixing the solutions slowly dissolved in the free acid, while at the same time crystals of $Ag_2TeO_4.2H_2O$ were formed upon the walls of the containing vessel.

In order to determine whether silver sulphate and silver tellurate are isomorphous, crystals of $Ag_2TeO_4.2H_2O$ were introduced into a saturated solution of silver sulphate and the solution allowed to evaporate. Silver sulphate crystallized out of the solution entirely independent of the silver tellurate. Silver sulphate (Ag_2SO_4) and silver tellurate ($Ag_2TeO_4.2H_2O$) are therefore not isomorphous. It may be stated that the tellurate of silver was decomposed by the solution to some extent, a few red crystals of a basic tellurate being formed.

The sulphate and selenate of silver are isomorphous, their axial ratios being as follows:

Silver sulphate $a:b:c=0.5712:1:1.238$

Silver selenate $a:b:c=0.5945:1:1.256$

However, these salts cannot properly be compared with the tellurate of silver since they are anhydrous, while silver tellurate contains two molecules of water.

In addition to the tellurate of silver described by Berzelius Oppenheim[32] describes a crystalline precipitate, which he obtained in small quantity by adding a saturated solution of telluric acid to a concentrated solution of silver nitrate. He states that it differs from any tellurate of silver obained by Berzelius in that it is crystalline and colorless. When exposed to the air it assumed a yellow color, according to Oppenheim. He states that he did not make a quantitative analysis of the substance but concluded that it was a double compound of silver tellurate and nitrate, since he found that it contained nitric and telluric acids together with silver.

[32] Jr. pr. Chem., Vol. 71, p. 266.

Gutbier[33] attempted to prepare the crystalline compound described by Oppenheim. When a concentrated solution of telluric acid is added to a concentrated solution of silver nitrate a red brown or yellow precipitate is formed. This precipitate is the only product that Gutbier obtained from such solutions.

When a solution of silver nitrate is added to a dilute solution of telluric acid no precipitate is formed. But if the solutions are sufficiently concentrated and an excess of telluric acid added, a yellow flocculent precipitate is formed in small quantity. If the solution and precipitate are allowed to remain together in a dark place at room temperature for a few hours the amorphous precipitate changes to straw yellow crystals of $Ag_2TeO_4.2H_2O$. This is the crystalline compound that Oppenheim obtained. Under the conditions of the experiment the crystals might easily be contaminated by silver nitrate.

ACID TELLURATES OF SILVER.

Berzelius states that concentrated solutions of $KHTeO_4$ and $K_2Te_4O_{13}$ react with concentrated solutions of silver nitrate to form the corresponding tellurate of silver. If the solution containing the precipitate is evaporated to dryness, a white earthy residue remains. Berzelius states that the acid tellurates are transformed to a brown basic tellurate of silver in dilute solutions.

Attempts were made to prepare the acid tellurate of silver described by Berzelius. It was not found possible to obtain precipitates having either the composition $AgHTeO_4$ or $Ag_2Te_4O_{13}$. The precipitates obtained in the manner described by Berzelius contain more telluric acid than is required by normal silver tellurate (Ag_2TeO_4), but upon remaining in the mother liquor for some hours they are largely transformed to crystalline $Ag_2TeO_4.2H_2O$. It would hardly be expected that a solution of $KHTeO_4$ would yield $AgHTeO_4$ with silver nitrate, when it is known that telluric acid and silver nitrate give the crystalline normal tellurate.

When concentrated solutions of $KHTeO_4$ and silver nitrate are brought together a bright yellow precipitate is formed. The

[33] l. c.

lemon yellow color of the amorphous precipitate is permanent, there being no tendency to form a brown basic tellurate in the medium present. Analysis of the precipitate obtained in this manner showed that it contained 46.6% silver and 32.9% tellurium. The ratio between the silver and telluric acid in the precipitate lies between those required by the formulae Ag_2TeO_4 and $AgHTeO_4$. Some of the precipitate was allowed to remain in the mother liquor for forty-eight hours. At the end of that time a large part of it had been converted into crystalline normal silver tellurate.

When a concentrated solution of silver nitrate is added to a solution of acid potassium tellurate made by dissolving potassium hydrate and telluric acid together in the proportions required by the formula $K_2Te_4O_{13}$ a bright yellow precipitate is formed. When left in contact with the mother liquor for some time the precipitate is largely changed to crystalline $Ag_2Te_4O.2H_2O$.

Analysis of the crystalline salt obtained in this manner gave the following results:

0.4006 grams gave 0.0329 grams H_2O and 0.2571 grams AgCl.

0.5384 grams with HCl liberated chlorine equivalent to 0.1555 grams Te.

Found H_2O, 8.21%; Te, 28.88%; Ag, 48.31%.

The silver tellurate prepared in this manner is not well crystallized. This is due to the fact that the precipitate is only slightly soluble in the mother liquor. The crystals darken only very slowly in direct sunlight.

When solutions of $HKTeO_4$ and silver nitrate are brought together in equimolecular proportions and the whole evaporated to dryness a white residue remains. Analysis of the residue obtained in this manner and washed with a little hot water shows that it contains telluric acid in excess of that required by normal silver tellurate. The residue also contains potassium. It is not possible to determine how much of the telluric acid is combined with the potassium, or how much of it is in the form of the free acid. Consequently no conclusion can be reached as to the exact composition of the silver tellurate in the residue. It is not feas-

ible to wash it thoroughly because of the decomposition that silver tellurate undergoes in the presence of water.

When crystals of normal or basic silver tellurate are boiled with a concentrated solution of telluric acid, a bright yellow amorphous precipitate is formed which is similar to the one obtained from solutions of acid potassium tellurate and silver nitrate.

BASIC SILVER TELLURATES.

Berzelius[34] describes two basic tellurates of silver, $3Ag_2O.2TeO_3$ and $3Ag_2O.TeO_3$, both of which were obtained as brown precipitates. He states that boiling water decomposes the normal tellurate of silver into $3Ag_2O.2TeO_3$ and telluric acid.

When a dilute solution of silver nitrate is added to a dilute solution of potassium tellurate, the dark yellow precipitate which is first formed quickly assumes a dark brown color. Berzelius found this dark brown precipitate to be $3Ag_2O.TeO_3$. He also prepared this compound by adding an ammonical solution of silver nitrate to a solution of normal silver tellurate in ammonia and evaporating the solution. The basic tellurate separates from the solutions as a brown black precipitate.

Gutbier[35] states that the precipitate formed by the action of silver nitrate on potassium tellurate may be completely changed to $3Ag_2O.TeO_3$ by long continued washing with cold water. He states that when the precipitate is washed with hot water the final product is $3Ag_2O.2TeO_3$. According to Gutbier this salt may be prepared by bringing together hot dilute solutions of silver nitrate and potassium tellurate.

$3Ag_2O.2TeO_3.3H_2O$.

In addition to the brown precipitates of $3Ag_2O.2TeO_3$ and $3Ag_2O.TeO_3$ already described, a crystalline tellurate of silver having the composition $3Ag_2O.2TeO_3.3H_2O$ was prepared during the progress of this work. When the precipitate obtained by

[34] l. c.
[35] l. c.

the double decomposition of moderately dilute solutions of silver nitrate and potassium tellurate assumes the crystalline condition, both yellow crystals of $Ag_2TeO_4.2H_2O$ and red crystals of $3Ag_2O.2TeO_3.3H_2O$ are formed. The relative amounts of these salts obtained depends largely upon the temperature of the solutions and their concentration. When the solutions are cold and concentrated but little of the basic salt is formed. On the other hand, if the solutions are very dilute and warm, it is possible to obtain the crystalline basic tellurate free from the normal salt.

Analysis of the red crystals gave the following results:

0.2812 grams gave 0.0653 grams Te
0.3763 grams gave 0.2917 grams AgCl
1.6094 grams gave 0.0797 grams H_2O

	Te	Ag	H_2O
Calculated for $3Ag_2O.2TeO_3.3H_2O$	23.18%	58.83%	4.90%
Found	23.22%	58.35%	4.95%

$3Ag_2O.2TeO_3.3H_2O$ crystallizes in ruby red, transparent crystals belonging to the monoclinic system. The crystals remain unchanged in cold water. They are gradually decomposed by boiling water with the formation of a brown residue, probably $3Ag_2O.TeO_3$. When boiled with an excess of a concentrated solution of telluric acid a bright yellow amorphous precipitate results which probably contains silver bi-tellurate ($AgHTeO_4$). The crystals are soluble in the same reagents that dissolve normal silver tellurate. In the sunlight the crystals become opaque and assume a copper color. When heated above 110° they lose water and become black, but all of the water is not given up until a temperature of about 200° is reached.

Just as it is possible to obtain crystals of hydrous normal silver tellurate by evaporation of solutions of silver tellurate under proper conditions, so it is possible by varying the conditions to obtain crystals of $3Ag_2O.2TeO_3.3H_2O$ directly from clear solutions. If a dilute solution of potassium tellurate is added to a large excess of silver nitrate containing a little free nitric acid, the solution filtered and allowed to evaporate at room temperature, red crystals of the basic salt are formed. The formation of crystals when the solution is evaporated is made possible by the

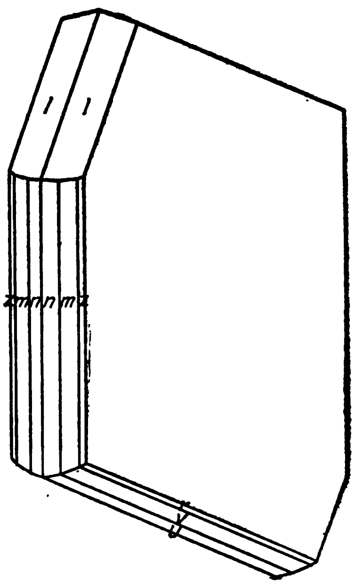
fact that the dilute nitric acid is saturated with silver tellurate dissolved from the amorphous precipitate. If the solution contains much nitric acid the silver tellurate is entirely decomposed with the formation of silver nitrate and telluric acid so that no crystals of the tellurate of silver appear when the solution is evaporated. Consequently a large volume of solution is necessary in order to obtain a small amount of the crystalline salt. Crystals of $3Ag_2O.2TeO_3.3H_2O$ have been repeatedly obtained in this manner, but only in small quantities.

Larger quantities of the salt have been prepared by double decomposition of solutions of silver nitrate and potassium tellurate and subsequent change of the amorphous precipitate thus obtained into the crystalline salt. If the solution contains no free acid the crystals form only in contact with the amorphous precipitate, since silver tellurate is insoluble in water. If, however, the solution contains a little free nitric or acetic acid, red crystals of $3Ag_2O.2TeO_3.3H_2O$ frequently form on the walls of the containing vessel. By working with dilute solutions at temperatures from 15° to 50° and using a large excess of silver nitrate, it has been found possible to obtain the red crystalline salt entirely free from yellow crystals of the normal salt. In most cases, however, more or less of the normal salt was formed. Both of the salts appear in distinct crystals. Their colors are so different that it is easy to ascertain when one salt contaminates the other and to remove it mechanically if it is present in small amount.

$3Ag_2O.2TeO_3.3H_2O$.

Monoclinic. Axes—a : b : c = 0.5290 : 1 : 0.2706. $\beta = 77° 12'$.

mm''',	$110 : 1\bar{1}0 = 125° 24'$.
ll,	$111 : 1\bar{1}1 = 154° 28'$.
nn''',	$210 : 2\bar{1}0 = 150° 00'$.
rb,	$13\bar{1} : 010 = 127° 43'$.
vb,	$12\bar{1} : 010 = 118° 00'$.
ub,	$11\bar{1} : 010 = 104° 33'$.
zz''',	$230 : 2\bar{3}0 = 104° 30'$.



$3Ag_2O.TeO_3$.

Silver orthotellurate ($3Ag_2O.TeO_3$) has not been obtained in the crystalline form. It is known only in the form of the brown amorphous precipitate described by Berzelius. The salt, somewhat contaminated by $3Ag_2O.TeO_3$, was obtained by adding a hot dilute solution of potassium tellurate to a solution of silver nitrate containing free nitric acid. Analysis of the precipitate, which had been thoroughly washed with hot water and dried over sulphuric acid, gave 72.9% silver. $3Ag_2O.TeO_3$ requires 74.3% silver.

The filtrate was allowed to evaporate at room temperature. Crystals of $3Ag_2O.2TeO_3.3H_2O$ formed in the solution.

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1. The precipitate obtained by double decomposition of a silver salt with telluric acid or a soluble tellurate, may vary in composition from a mixture containing more telluric acid than Ag_2TeO_4 to $3Ag_2O.TeO_3$, depending upon the conditions in the medium.
2. It has not been found possible to obtain the acid tellurates of silver, $AgHTeO_4$ and $Ag_2O.4TeO_3$ described by Berzelius.
3. Silver forms two crystalline tellurates—$Ag_2TeO_4.2H_2O$, which appears as yellow crystals belonging to the orthorhombic system, and $3Ag_2O.2TeO_3.3H_2O$, whose crystals are red and belong to the monoclinic system.
4. The crystalline compound that Oppenheim described as a double salt of silver tellurate and silver nitrate, is $Ag_2TeO_4.2H_2O$.
5. No sulphates or selenates of silver have been prepared that are analogous to the crystalline tellurates of silver.

THE TELLURATES OF POTASSIUM.

NORMAL POTASSIUM TELLURATE.

Berzelius[36] states that normal potassium tellurate can be prepared by treating potassium carbonate with telluric acid. These compounds were dissolved together in equimolecular quantities and the solution evaporated to dryness. The residue was dissolved in water and the solution evaporated *in vacuo* over sulphuric acid until a crystalline crust formed. According to Berzelius this crust consisted of normal potassium tellurate. If the solution is evaporated at a moderate temperature a gummy mass is deposited.

Gutbier[37] states that he was not able to obtain normal potassium tellurate by this method.

Experiments were undertaken to ascertain whether normal potassium tellurate could be obtained by this method. It was found that solutions made by dissolving equivalent quantities of potassium carbonate and telluric acid in water always yield a gummy mass when they are evaporated *in vacuo*.

Potassium tellurate crystallizes from its solutions if they are allowed to evaporate very slowly. This separation of the crystalline salt is aided by the addition of a few crystals of the salt. When solutions, made according to the directions of Berzelius, are evaporated in this manner no crystals are formed. The gummy mass even separates around the crystals of $K_2TeO_4.5H_2O$, introduced into the solution. This pasty mass evolves carbon dioxide when treated with hydrochloric acid. The same result is obtained if the solution is cooled to zero instead of evaporated.

That all of the carbon dioxide appearing in the gummy mass had not been absorbed from the air is shown by the following experiment: 1.42 grams of anhydrous potassium carbonate and 2.37 grams of telluric acid were dissolved in a little water. The solution was at once evaporated to dryness over a free flame.

[36] Pogg. Ann., Vol. 32, p. 579.
[37] Zeit. f. anorg. Chem., Vol. 31, p. 340.

The residue copiously evolved carbon dioxide when treated with hydrochloric acid. It is evident that telluric acid cannot replace all of the carbonic acid in an equimolecular quantity of potassium carbonate. This fact is in harmony with the fact, observed by Berzelius, that carbon dioxide reacts on normal potassium tellurate to form acid potassium tellurate, $KHTeO_4$, and potassium carbonate.

No carbon dioxide is evolved when saturated solutions of acid potassium tellurate ($KHTeO_4$) and potassium carbonate are brought together at 95° in the proportion of two molecules of the acid tellurate to one of the carbonate. $KHTeO_4$ is more soluble in a solution of potassium carbonate than in water.

$K_2TeO_4.5H_2O$.

Berzelius[38] prepared crystalline $K_2TeO_4.5H_2O$ from concentrated solutions of potassium hydrate and telluric acid in the following manner: A solution of potassium hydrate was added to a solution of telluric acid until a permanent precipitate formed, indicating the presence of an excess of the alkali. The gummy precipitate was dissolved by warming the solution. Crystals of $K_2TeO_4.5H_2O$ separated from the solution upon cooling it to zero. The salt is decomposed by carbon dioxide with the formation of $KHTeO_4$ and potassium carbonate.

Gutbier[39] obtained $K_2TeO_4.5H_2O$ in the form of long slender needles by employing the method of preparation used by Berzelius. Gutbier states that it is very difficult to obtain the salt free from adhering alkali since it cannot be recrystallized without adding free alkali to the solution of the salt.

Retgers[40] describes a second crystalline tellurate of potassium ($K_2TeO_4.2H_2O$) which he prepared by dissolving telluric acid in a concentrated boiling solution of potassium hydroxide and allowing the solution to cool slowly. He states that crystals of $K_2TeO_4.2H_2O$ are isomorphous with those of $K_2OsO_4.2H_2O$.

[38] l. c.
[39] l. c.
[40] Zeit. f. phys. Chem., Vol. 10, p. 536.

Gutbier[41] also prepared $K_2TeO_4.2H_2O$ by dissolving telluric acid in hot concentrated potassium hydroxide and cooling the solution. He found the salt to be isomorphous with $K_2OsO_4.2H_2O$.

Nandl and von Lang[42] describe crystalline anhydrous potassium tellurate (K_2TeO_4) which they found to be isomorphous with potassium sulphate. Gutbier, Rammelsberg, Staudenmaier, and Retgers have been unable to prepare the anhydrous crystalline tellurate.[43]

$K_2TeO_4.5H_2O$ may be obtained in the form of crystals by slow evaporation of solutions of the salt at room temperatures. Whenever solutions of potassium tellurate are allowed to evaporate *in vacuo* over sulphuric acid they solidify to a gummy mass which does not become crystalline until it is dry. In order to bring about slower evaporation of the solution the loosely covered dish containing the solution may be placed in a desiccator over sulphuric acid. The desiccator should be filled with air freed from carbon dioxide to prevent the formation of potassium carbonate and acid potassium tellurate. Potassium tellurate has been repeatedly crystallized from its solutions in this manner. The solution may be concentrated rapidly until its specific gravity is about 1.2 and then crystallized by slow evaporation. The fact that potassium tellurate is very soluble renders it somewhat difficult to obtain a nicely crystallized product. Frequently the crystals form radiating clusters but in other cases the crystals are distinct. Solutions of potassium tellurate that have become supersaturated can frequently be made to crystallize by adding a few crystals of $K_2TeO_4.5H_2O$ and preventing further evaporation by closely covering the solution. Even under these conditions crystallization proceeds slowly.

Crystals of $K_2TeO_4.5H_2O$ may be obtained by slow evaporation of the solution resulting from the double decomposition of equivalent quantities of normal silver tellurate and potassium bromide solution. This may be readily accomplished in the following manner. The potassium bromide and silver tellurate are

[41] l. c.
[42] Wiener Akad. Ber., Vol. 43, p. 117.
[43] Gutbier, Studien über das Tellur., p. 36.

thoroughly ground together, treated with a little warm water and again triturated. After standing for some time in an atmosphere free from carbon dioxide the solution is filtered and crystallized in the manner described above.

Analysis of crystals obtained in this manner gave the following results:

0.9742 grams gave 0.2420 grams H_2O.

0.9742 grams gave 0.4010 grams KCl.

0.2839 grams with hydrochloric acid liberated chlorine equivalent to 0.1001 grams Te.

	Calculated for $K_2TeO_4.5H_2O$	Found
H_2O	25.01	24.84
K	21.76	21.60
Te	35.45	35.26

Crystals of $K_2TeO_4.5H_2O$ are soft and crumble under a slight pressure. Solutions of the salt are alkaline to litmus and attack glass.

Solutions of potassium tellurate containing two molecules of free potassium hydroxide to one of the tellurate yield crystals of $K_2TeO_4.5H_2O$ when evaporated slowly. The yield is small on account of the free alkali in the solution. Solutions of this kind were evaporated in order to ascertain whether potassium tellurate would crystallize with two or five molecules of water under these conditions.

Crystals that had been washed with water and dried with filter paper gave the following results upon analysis:

1.1936 grams gave 0.3000 grams H_2O.

1.1936 grams gave 0.4916 grams KCl.

0.6443 grams with hydrochloric acid liberated chlorine equivalent to 0.2306 grams Te.

	Calculated for $K_2TeO_4.5H_2O$	Found
H_2O	25.01	25.15
K	21.75	21.63
Te	35.45	35.79

$K_2TeO_4.2H_2O$.

This salt was obtained in the form of distinct crystals by dissolving telluric acid in a hot concentrated solution of potassium hydrate and allowing the solution to cool. The yield was very small.

Analysis of the salt after having been washed with water at zero and dried for a day over calcium chloride gave the following result:

1.4806 grams gave 0.1767 grams of water.

Calculated for $K_2TeO_4.2H_2O$	11.47
Found	11.93

When the solution of potassium hydrate, from which the crystals of $K_2TeO_4.2H_2O$ had been removed, was diluted a copious amount of $K_2TeO_4.5H_2O$ separated as small crystals. This fact indicates that the formation of the dihydrate in the concentrated solution is due to the dehydrating effect of the strong alkali. It is also evident that $K_2TeO_4.5H_2O$ is less soluble in a dilute solution of potassium hydrate than $K_2TeO_4.2H_2O$ is in a concentrated solution.

ACID TELLURATES OF POTASSIUM.

Berzelius states that potassium bitellurate ($KHTeO_4$) may be obtained from equivalent quantities of telluric acid and potassium carbonate, but that it is produced with greater certainty by dissolving potassium carbonate and telluric acid in a small amount of hot water in such proportions that there shall be two molecules of telluric acid present to one of potassium carbonate. When such a solution is cooled the bitellurate of potassium separates upon the walls of the containing vessel in granular tufts. The formula $K_2O.2TeO_3.4H_2O$ is assigned to the crystalline salt.

Berzelius states that potassium quadrotellurate ($K_2O.4TeO_3$) can be obtained by the same method as the bitellurate. In the case of the quadrotellurate, however, telluric acid and potassium carbonate were dissolved in the proportion of four molecules of the former to one of the latter. The formula $K_2O.4TeO_3.4H_2O$

is assigned to the crystalline salt. Berzelius states that these salts may also be obtained by treating a solution of normal potassium tellurate with the requisite amount of an acid (nitric or sulphuric) to withdraw potassium.

Berzelius also describes a yellow insoluble quadrotellurate of potassium obtained by heating either $K_2O.2TeO_3$ or $K_2O.4TeO_3$. He states that this compound may also be obtained by heating telluric acid with potassium nitrate at a temparature below a red heat. The compound is insoluble in cold nitric, hydrochloric, and sulphuric acids, and potassium hydrate.

$KHTeO_4$.

A tellurate of potassium containing more telluric acid than $KHTeO_4$ cannot be obtained by the action of carbon dioxide on normal potassium tellurate. When carbon dioxide is passed into a concentrated solution of potassium tellurate a white precipitate of potassium bitellurate ($KHTeO_4$) is immediately formed. The precipitate may settle as a gummy mass, but it becomes granular when cooled to zero. The composition of this precipitate is not changed by prolonged contact with carbon dioxide. $KHTeO_4$, obtained in this manner, was repeatedly covered with distilled water, cooled to zero, and treated with carbon dioxide.

Analysis of the residue, after having been dried with filter paper, gave the following results:

0.5428 grams with hydrochloric acid liberated chlorine equivalent to 0.2415 grams Te.

0.9906 grams gave 0.2511 grams KCl.

1.5444 grams gave 0.3492 grams H_2O.

Found 44.49% Te; 13.30% K; and 22.62% H_2O.

After deducting the water, some of which was evidently held mechanically, the values obtained for potassium and tellurium correspond closely with those required by the formula $K_2O.2TeO_3$. In another experiment 18% of water was obtained from a sample dried with filter paper, while the same sample gave 13.2% of water after having been dried over phosphorus pentoxide for several days. The calculated value for water in $KHTeO_4.2H_2O$ is

16.8%, and for $KHTeO_4.1\frac{1}{2}HO$ (or $K_2O.2TeO_3.4H_2O$) 13.9%. The latter formula is the one assigned to the bitellurate by Berzelius.

Potassium bitellurate may be obtained in the form of a transparent crystalline crust by slow evaporation of its solutions. It is only sparingly soluble in water at 0°; but is readily soluble in boiling water. It is alkaline to litmus.

When a solution of potassium bicarbonate is added to a concentrated solution of normal potassium tellurate a white precipitate is formed. The precipitate appears flocculent when it is first formed, but it settles as a gummy mass. The precipitate is so soluble in the menstruum present that a large amount of potassium tellurate is required to obtain a small amount of the solid material. The precipitate is probably potassium bitellurate. Its solubility in the menstruum may be due to potassium carbonate formed by the reaction—

$$KHCO_3 + K_2TeO_4 = KHTeO_4 + K_2CO_3.$$

This reaction is in harmony with the fact, mentioned above, that potassium bitellurate does not react with potassium carbonate to give carbon dioxide. The ready formation of potassium bitellurate may be due largely to the insolubility of the compound, but from the facts that have been mentioned it seems probable that telluric acid is a weaker acid than carbonic.

$K_2O.3TeO_3.5H_2O.$

When solutions made by dissolving potassium carbonate and telluric acid together in water in the proportion of one molecule of the carbonate to four of the acid are evaporated, a white granular precipitate of $K_2O.3TeO_3.5H_2O$ is deposited. Analysis of the salt, after having been dried for eleven days over phosphorus pentoxide, gave the following results:

1.6971 grams gave 0.2075 grams H_2O.

1.6971 grams gave 0.3495 grams KCl.

1.3340 grams gave (with HCl) chlorine equivalent to 0.7207 grams Te.

	Calculated for $K_2O.3TeO_3.5H_2O$	Found
H_2O	12.65	12.22
K	11.01	11.06
Te	53.83	54.02

The salt reacts alkaline to litmus. Like the bitellurate it is much more soluble in hot water than in cold.

This acid salt may be obtained by dissolving potassium carbonate and telluric acid together in the ratio of one molecule of potassium carbonate to three of telluric acid.

MERCUROUS TELLURATES.

Berzelius[44] describes normal mercurous tellurate (Hg_2TeO_4) as a yellow-brown precipitate obtained by adding powdered mercurous nitrate to a solution of potassium tellurate. When a solution of mercurous nitrate is used instead of the powdered salt, the yellow-brown precipitate gradually changes to a pale yellow color. Berzelius states that this change in color is probably due to the formation of the bitellurate of mercury ($HgHTeO_4$) brought about by the free acid in the solution of the mercury salt.

Oppenheim[45] states that when a concentrated solution of mercurous nitrate is treated with telluric acid a white cheesy precipitate forms which becomes yellow in the air. He considers this precipitate a double salt of mercurous nitrate and tellurate analogous to the double compounds of silver and lead that he describes.

The precipitates obtained by double decomposition of solutions of mercurous nitrate and a soluble tellurate or telluric acid may vary in composition from $HHgTeO_4$ to $3HgO.2TeO_3$.

However, any precipitate of mercurous tellurate may be changed to crystals of $HHgTeO_4.3H_2O$ by treatment with a cold concentrated solution of telluric acid. This acid tellurate is not only the only crystalline mercurous tellurate that has been prepared, but it is the only mercurous tellurate of definite composition that has been obtained during the progress of this work.

[44] Pogg. Ann., Vol. 32, p. 577.
[45] Jr. f. pr. Chem., Vol. 71, p. 266.

Mercurous tellurate is a striking example of a salt of a weak acid and a weak base. Slight variations of the conditions under which a salt is placed may bring about a change in its composition, causing it to become either more acid or more basic. This, together with the fact that the salt is readily decomposed giving free mercury and mercuric tellurate, renders the preparation of the tellurates of monovalent mercury somewhat difficult.

$HHgTeO_4.3H_2O$.

This crystalline salt may be obtained either by double decomposition of solutions of mercurous nitrate and telluric acid or by the action of telluric acid upon mercurous oxide.

When mercurous oxide is treated with a cold concentrated solution of telluric acid it is slowly attacked and colorless crystals of $HHgTeO_4.3H_2O$ are formed. As the resulting crystals are mixed with the unattacked oxide, this is not a suitable method for the preparation of the salt in pure condition.

Large amounts of the salt may be conveniently prepared by treating a solution of mercurous nitrate with telluric acid and subsequent change of the precipitate to the crystalline salt. When a solution of telluric acid is added to a solution of mercurous nitrate a bright yellow precipitate is formed. If a large excess of telluric acid is added, the yellow precipitate becomes nearly white and slowly changes to colorless crystals of $HHgTeO_4.3H_2O$. The presence of considerable free nitric acid in the solution aids greatly in the formation of crystals of the salt. Under these conditions crystals frequently form on the walls of the containing vessel.

Analysis of the colorless crystals gave the following results:

1.9265 grams gave 0.2717 grams H_2O.

0.8459 grams gave 0.4358 grams HgS.

1.2416 grams with hydrochloric acid liberated chlorine equivalent to 0.3501 grams Te.

	Calculated for $HHgTeO_4.3H_2O$	Found
Hg	44.78	44.40
Te	28.57	28.21
H_2O	14.11	14.11

For the estimation of the mercury, all of which was present in the mercurous condition, the salt was treated with dilute hydrochloric acid and the precipitated mercurous chloride oxidized with bromine water. The mercury was precipitated with hydrogen sulphide.

Tellurium was estimated by decomposing the salt with hydrochloric acid, absorbing the liberated chlorine in a solution of potassium iodide and titrating the free iodine with sodium thiosulphate. The chlorine absorbed by the solution of potassium iodide represents only a portion of the chlorine liberated by the oxidation of the hydrochloric acid. When the tellurate is treated with hydrochloric acid in the cold, mercurous choride is precipitated. Upon heating the solution the chlorine formed by the oxidation of the hydrochloric acid converts the mercurous chloride into mercuric chloride. The amount of chlorine thus reduced was calculated and added to the amount absorbed by the iodide solution in order to determine the amount of tellurium in the salt. The reactions involved may be represented as follows:

$$2HHgTeO_4 + 2HCl = Hg_2Cl_2 + 2H_2TeO_4 + H_2O.$$
$$2H_2TeO_4 + 12HCl = 2TeCl_4 + 8H_2O + 2Cl_2.$$
$$Hg_2Cl_2 + Cl_2 = 2HgCl_2.$$

One-half of the chlorine liberated during the reaction is reduced by the mercurous chloride in the solution.

$HgHTeO_4.3H_2O$ crystallizes in the triclinic system. It is insoluble in water but soluble in dilute acetic or nitric acid. Ammonium hydroxide reacts with the salt to form a black precipitate. Sunlight blackens the salt, but it is stable in the air if protected from the light. Crystals of the salt have been preserved in closed tubes for a year without losing their transparency or changing in any respect. With boiling water the crystals quickly decompose, telluric acid and a yellow amorphous tellurate being formed. An excess of cold concentrated mercurous nitrate solution brings about the same result. If the yellow basic precipitate is treated with an excess of telluric acid it may be changed to crystals of $HHgTeO_4.3H_2O$. When strongly compressed between steel rolls the salt detonates and assumes a brown color. The amorphous mercurous tellurates possess the same property. It has been observed that when a glass rod is drawn over the wet

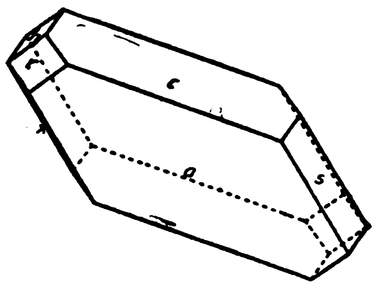
precipitate obtained by bringing together solutions of mercurous nitrate and potassium tellurate, it changes from a yellow to a brown color. The same change may be brought about by pressing the precipitate between layers of filter paper.

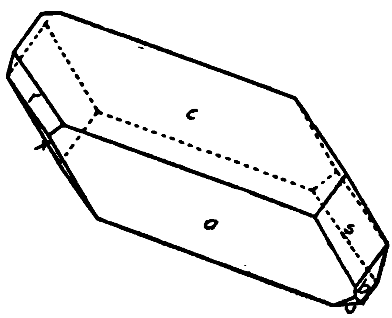
$HHgTeO_4.3H_2O$.

Triclinic. Axes—a : b : c = 1.044 : 1 : 1.055

$\alpha = 100° 30'$; $\beta = 106° 03'$; $\gamma = 103° 59'$.

ca,	$001 : 100$	$= 109° 38'$.
ab,	$100 : 010$	$= 108° 00'$.
cb,	$001 : 010$	$= 105° 30'$.
cs,	$001 : 011$	$= 141° 45'$.
cx,	$001 : \bar{1}11$	$= 127° 07'$.
sx,	$011 : \bar{1}11$	$= 141° 30'$.
c′r,	$00\bar{1} : \bar{1}1\bar{1}$	$= 131° 32'$.
as,	$100 : 011$	$= 114° 05'$.
bx,	$010 : \bar{1}11$	$= 130° 15'$.
c′h,	$00\bar{1} : 01\bar{1}$	$= 126° 08'$.
hs,	$01\bar{1} : 011$	$= 92° 23'$.
ub,	$22\bar{3} : 010$	$= 133° 25'$.
uc′,	$22\bar{3} : 00\bar{1}$	$= 103° 30'$.
rb,	$\bar{1}1\bar{1} : 010$	$= 106° 00'$.
xa′,	$\bar{1}11 : \bar{1}00$	$= 104° 25'$.





Other Mercurous Tellurates.

All attempts to prepare normal mercurous tellurate in the crystalline form have been unsuccessful. Indeed, it has not been found possible to obtain an amorphous tellurate of mercury having exactly the composition Hg_2TeO_4. The salt is likely to be contaminated by either a basic or an acid tellurate of mercury, depending upon the conditions in the solution. The preparation of the salt is still further complicated by the fact that the precipitate obtained by double decomposition of mercurous nitrate and potassium tellurate contains nitric acid which it is difficult to remove by washing. Moreover, long continued treatment with water decomposes the precipitate.

When a large excess of a cold concentrated solution of potassium tellurate is added to a concentrated solution of mercurous nitrate the yellow precipitate, which is first formed, quickly changes to a brown. The precipitate is slimy and difficult to wash. It approximates Hg_2TeO_4 in composition.

Impure $3Hg_2O.2TeO_3$ may be obtained as a yellow amorphous precipitate by treating a hot dilute solution of potassium tellurate with an excess of mercurous nitrate solution and washing the precipitate with hot water. It is hardly possible to obtain the precipitate free from nitric acid.

A mercurous tellurate analogous or silver orthotellurate (Ag_6TeO_6) has not been prepared. When the bulky yellow precipitate, obtained by treating a hot dilute solution of potassium tellurate with an excess of mercurous nitrate solution is washed with hot water and boiled for some time in water it is decomposed giving free mercury. The precipitate may be boiled for several hours without changing in appearance, but at length it settles as a heavy brown granular powder containing free mercury. This change may be hastened by rubbing some of the precipitate against the side of the beaker with a glass rod.

When the brown powder is heated with hydrochloric acid elementary tellurium is precipitated.

MERCURIC TELLURATES.

Berzelius describes mercuric tellurate ($HgTeO_4$) as a white flocculent precipitate.

Divalent mercury forms two salts with telluric acid, mercuric orthotellurate (Hg_3TeO_6) and normal mercuric tellurate ($HgTeO_4$), both of which have been prepared in crystalline form. $HgTeO_4$ may be obtained as a white flocculent precipitate as described by Berzelius. Under favorable conditions it crystallizes with two molecules of water, giving $HgTeO_4.2H_2O$. The intermediate compound $3HgO.2TeO_3$ has not been isolated, although there are indications that it may exist. All precipitates of mercuric tellurate, whether crystalline or amorphous, show a strong tendency in the presence of water to change to mercuric orthotellurate. This property of mercuric tellurate renders it difficult to prepare $HgTeO_4$ in pure condition.

Mercuric Orthotellurate—Hg_3TeO_6.

When an excess of mercuric nitrate is added to a hot dilute solution of potassium tellurate, a heavy yellow granular precipitate of mercuric orthotellurate is formed. In order to obtain this salt in crystalline form, a somewhat different method of procedure must be employed.

If a cold concentrated solution of mercuric nitrate is added to a concentrated solution of potassium tellurate made acid with nitric acid, a white flocculent precipitate of $HgTeO_4$ is formed. At room temperatures a portion of the precipitate usually assumes a yellow color immediately, probably due to the formation of a basic salt. If the acid solution containing this white or yellow flocculent precipitate is allowed to stand undisturbed for several days the precipitate is largely converted into transparent amber colored crystals of Hg_3TeO_6. Frequently the walls of the containing vessel are covered with crystals that have separated from the acid solution. In many cases the amber colored crystals form in contact with the white amorphous precipitate, but

in all cases the crystals are entirely distinct from the precipitate.

Hg_3TeO_6 crystallizes in the isometric system, the predominating form being the dodecahedron. Combinations of the cube and dodecahedron are frequent, while many crystals show a broad octahedral face on which the crystal has grown. Single crystals have been obtained which are over an eighth of an inch in diameter. The crystals contain a little nitric acid and about 0.6% of water. This is considerably less than one-half of a molecule of water to one of Hg_3TeO_6.

The crystals are insoluble in water and unchanged by boiling with water. They are soluble in nitric acid but more readily soluble in hydrochloric acid. Hot potassium hydrate precipitates mercuric oxide. The powdered salt does not change in composition when kept in contact with a cold saturated solution of telluric acid for 48 hours.

When heated the salt assumes a red color, but it regains its original color upon cooling. The crystals are not altered by heating to 140°.

Analysis of the salt, after having been dried over phosphorus pentoxide for several days, gave the following results:

4.6696 grams gave 0.0279 grams H_2O.

1.7853 grams gave 1.4940 grams HgS.

1.0894 grams with hydrochloric acid liberated chlorine equivalent to 0.1727 grams Te.

Found	72.13% Hg	15.85% Te	0.59% H_2O

The value obtained for tellurium is about 0.5% too high. This discrepancy is due to the presence of a little nitric acid in the crystals.

The corresponding sulphate of mercury, Hg_3SO_6, exists as turpeth mineral. This compound may be prepared as a heavy yellow powder or as yellow crystals by treating the normal sulphate with water. In color the sulphate is very similar to the tellurate, but it does not crystallize in the isometric system.

Amorphous Hg_2TeO_4.

When concentrated solutions of mercuric nitrate and potassium tellurate or telluric acid are brought together at zero a white

flocculent precipitate of mercuric tellurate is formed. The precipitate is quickly decomposed by water at room temperature into telluric acid and basic mercuric tellurate. This decomposition goes on even when the precipitate is washed with water at zero; consequently it is impossible to obtain a pure white product in suitable condition for analysis. The precipitate remains white indefinitely in a saturated solution of telluric acid at room temperature.

Analysis of the light yellow powder obtained by washing the white precipitate with water at 0° showed that it approximates $HgTeO_4$ in composition.

Crystalline $HgTeO_4.2H_2O$.

If the white precipitate of mercuric tellurate formed by mixing concentrated solutions of mercuric nitrate and potassium tellurate containing free nitric acid, is allowed to remain undisturbed in the mother liquor for several days at room temperature, nearly all of it is converted into crystalline Hg_3TeO_6. In some cases colorless crystals of $HgTeO_4.2H_2O$ were obtained mixed with the amber colored crystals of mercuric orthotellurate.

Analysis of the colorless crystals gave the following results:

0.2413 grams gave 0.0202 grams H_2O;

0.2413 grams gave 0.0887 grams TeO_2;

	Calculated for $HgTeO_4.2H_2O$	Found
Te	29.84	29.39
H_2O	8.41	8.37

$HgTeO_4.2H_2O$ appears as transparent crystals belonging to the orthorhombic system. It is slowly decomposed by cold water. Boiling water quickly decomposes it into telluric acid and basic mercuric tellurate.

Copper Orthotellurate, Cu_3TeO_6.

When a solution of copper nitrate is treated with a solution of potassium tellurate a green flocculent precipitate of copper tellurate is formed. Berzelius describes this compound as normal copper tellurate ($CuTeO_4$). If the precipitate is boiled for some

hours with water it is converted into copper orthotellurate, which settles as a heavy green powder. It is insoluble in water but soluble in ammonia, potassium cyanide, and acetic, hydrochloric, and nitric acids.

Analysis of the green powder after having been dried over phosphorus pentoxide for a week gave the following result:

0.6675 grams heated with hydrochloric acid liberated chlorine equivalent to 0.2069 grams tellurium.

Cu_3TeO_6 requires 30.79% tellurium; found 31.00%.

Numerous attempts were made to prepare copper tellurate in crystalline form, but none were successful. Copper hydrate was treated with an excess of telluric acid; the resulting tellurate of copper was allowed to remain in the solution for several weeks. Likewise the precipitate obtained by bringing together solutions of potassium tellurate and copper nitrate was allowed to remain in mother liquors of varying composition for weeks. In no case were any crystals of copper tellurate formed.

Zinc Orthotellurate, Zn_3TeO_6.

The white flocculent precipitate obtained by bringing together solutions of zinc nitrate and potassium tellurate may be changed into a heavy granular precipitate of Zn_3TeO_6 by long continued treatment with hot water.

Analysis of the powder prepared in this manner and dried over phosphorus pentoxide for a week gave the following result: 0.6331 grams with hydrochloric acid liberated chlorine equivalent to 0.1940 grams tellurium. Calculated for Zn_3TeO_6, 30.40% tellurium; found 30.64%.

Zn_3TeO_6 is insoluble in water but soluble in acetic, nitric, hydrochloric, and sulphuric acids.

Gutbier[46] prepared zinc tellurate in the form of a white insoluble precipitate by bringing together solutions of potassium tellurate and zinc chloride. He does not give the composition of the tellurate of zinc that he obtained in this manner.

[46] Zeit. f. anorg. Chem., Vol. 31, p. 349.

Attempts were made to prepare zinc tellurate in crystalline form by allowing the amorphous salt to remain in contact with mother liquors of various compositions. The results were all negative.

GOLD TELLURATE.

No tellurate of gold has been prepared. From the experiments that have been made in an attempt to prepare this salt it seems probable that water immediately decomposes the salt if it is formed in aqueous solutions.

When a solution of gold chloride is added to normal silver tellurate suspended in water, silver chloride and gold oxide are precipitated.

When solutions of normal potassium tellurate and gold chloride are brought together and the resulting solution allowed to evaporate over sulphuric acid, yellow crystals of potassium chlor-aurate are formed. No tellurate of gold separates from the solution.

The fact that gold chloride takes up potassium from potassium tellurate to form potassium chlor-aurate is a good illustration of the weak affinity that telluric acid exerts towards bases.

SEPARATION OF GOLD FROM TELLURIUM.

While working with gold and telluric acid it became necessary to separate gold from tellurium. It was found that nitrous acid would not reduce either telluric or tellurous acids. Nitrous acid completely reduces gold from its solutions.[47] Gold may be separated from tellurium in dilute acid solution by the addition of potassium nitrate. After filtering out the precipitated gold, tellurium may be determined in the filtrate by precipitation with sulphur dioxide.

[47] Fischer, Pogg. Ann., Vol. 17, p. 480.

SUMMARY.

1. Telluric acid forms ortho-tellurates of the type M'_6TeO_6 with a number of the metals. Ag_6TeO_6, Hg_3TeO_6, Zn_3TeO_6, and Cu_3TeO_6 have been prepared. The normal tellurates (e. g. Ag_2TeO_4) of these metals are changed to the ortho compounds by treatment with water.

2. The crystalline normal tellurates that have been prepared, viz.: $Ag_2TeO_4.2H_2O$, $Rb_2TeO_4.3H_2O$, $HgTeO_4.2H_2O$, $Cs_2TeO_4.3H_2O$, $Na_2TeO_4.2H_2O$, and $K_2TeO_4.2H_2O$,[48] may be considered acid salts of orthotelluric acid of the types $M'_2H_4TeO_6$ and $M'_2H_4TeO_6.H_2O$.

3. Silver forms two crystalline tellurates—$Ag_2O.TeO_3.2H_2O$ and $3Ag_2O.2TeO_3.3H_2O$. The former salt is yellow and crystallizes in the orthorhombic system; the latter is red and crystallizes in the monoclinic system. Both of these salts may be considered acid salts of orthotelluric acid. No selenate or sulphate of silver is known that is isomorphous with either of these salts.

4. $HgHTeO_4.3H_2O$ crystallizes in the triclinic system. It is the only crystalline mercurous tellurate that has been prepared.

5. Two crystalline salts of divalent mercury have been prepared, viz.: Hg_3TeO_6 and $HgTeO_4.2H_2O$. The former appears in the form of amber colored crystals belonging to the isometric system; the latter is white and crystallizes in the orthorhombic system.

6. The crystalline compound described by Oppenheim as a double salt of silver nitrate and tellurate is normal silver tellurate ($Ag_2TeO_4.2H_2O$).

7. It has not been found possible to prepare the acid tellurates of silver described by Berzelius.

8. Potassium tellurate may be prepared in crystalline form by slow evaporation of its solution, provided care is exercised to prevent supersaturation of the solution.

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[48] Potassium forms a second tellurate—$K_2TeO_4.5H_2O$.

9. Telluric acid does not completely replace the carbonic acid in an equivalent quantity of potassium carbonate. Crystalline normal potassium tellurate cannot be obtained from potassium carbonate and telluric acid as described by Berzelius.

10. Although telluric acid is a weak acid, hot concentrated solutions of it attack mercury, silver, lead, tin, arsenic, antimony, bismuth, nickel, zinc, aluminum, and cadmium.

11. There are no well authenticated cases of isomorphism between sulphates and tellurates or between selenates and tellurates.

This work was undertaken at the suggestion of Professor Lenher and carried out under his guidance. I wish to take this opportunity of expressing my thanks for the inspiration that I have received from him in the laboratory as well as in the classroom.